

# REPORT DOCUMENTATION PAGE

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MEMORANDUM FOR PRS (In-House Publication)

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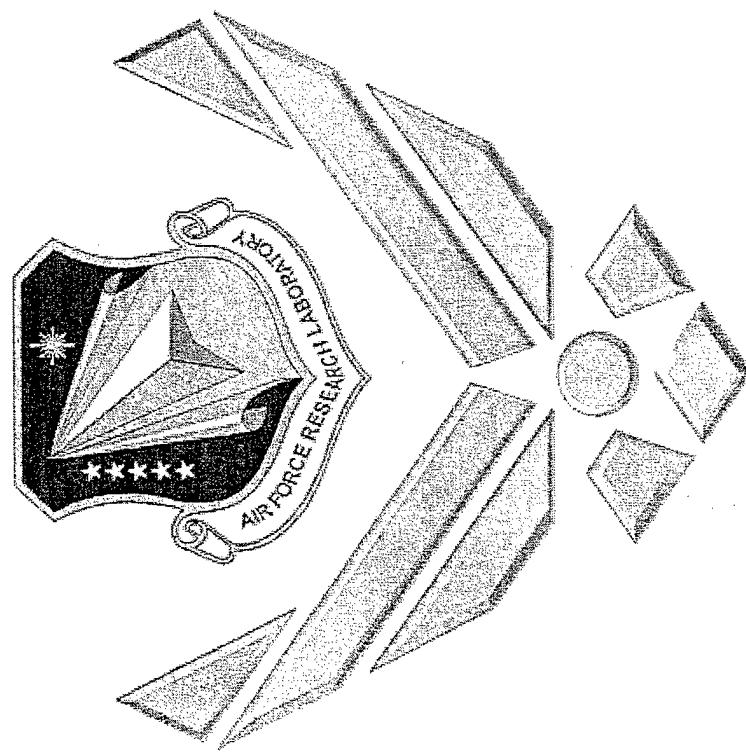
24 April 2002

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-087**  
Brent Viers (PRSM), "Thin Film Properties of POSS"

**SAMPE Presentation** (Statement A)  
**(Long Beach, CA, 10-16 May 2002) (Deadline: 16 May 2002)**

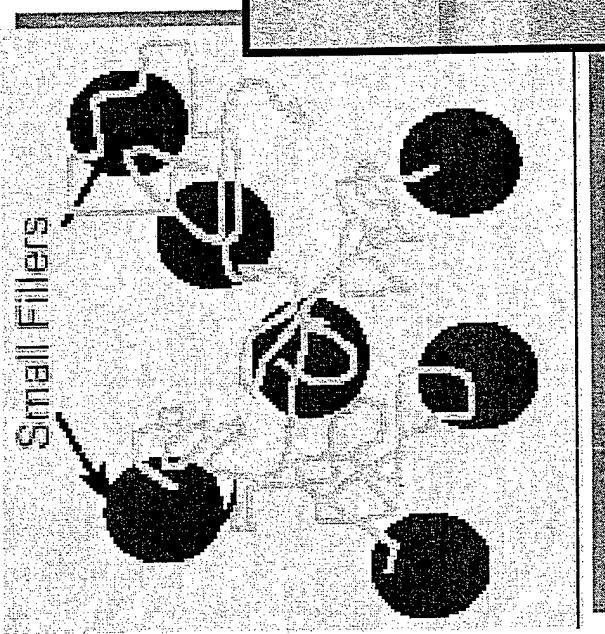
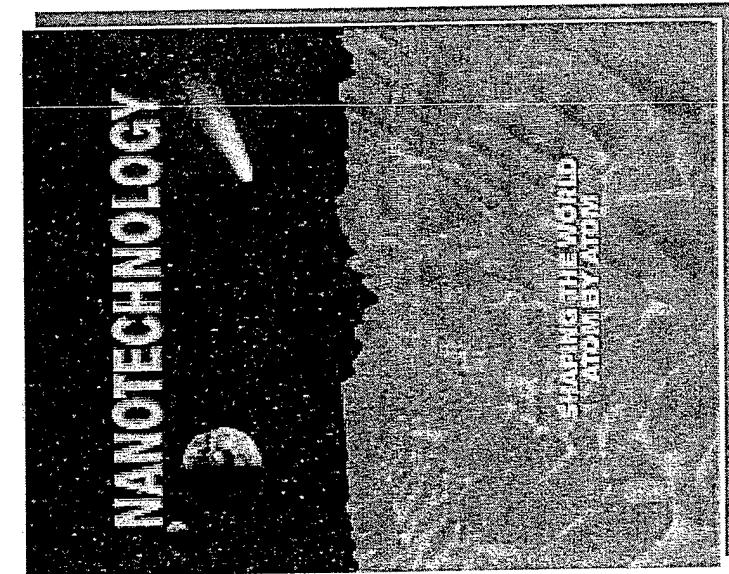
# Thin Film Properties of POSS

DISTRIBUTION STATEMENT A  
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Dr. Brent Viers  
POSS Polymer Group Leader  
Air Force Research Laboratory  
Propulsion Materials (AFRL/PRSM)  
[Brent.viers@edwards.af.mil](mailto:Brent.viers@edwards.af.mil)

# Inorganic-Organic Hybrids = Nanotechnology



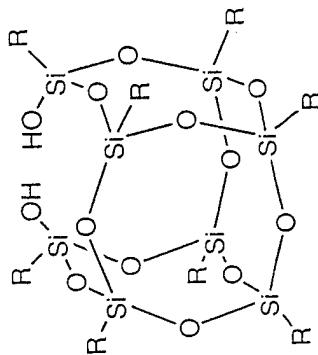
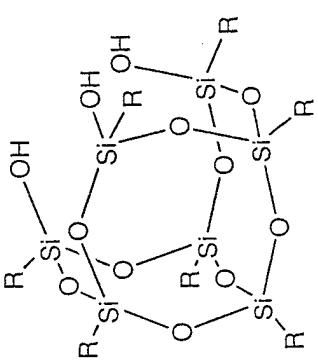
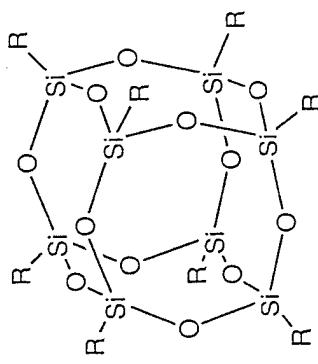
National Nanotechnology  
Initiative  
<http://www.nano.gov>

‘Perpetual Plastics: By adorning  
the polymer structure of  
synthetic plastic with ceramic  
nanoparticles, researchers  
hope to develop new substances  
that will last far longer’

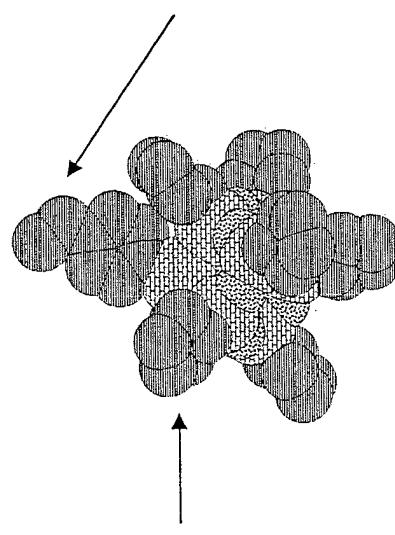
Mark Gordon, Iowa State U

# What is POSS?

POSS=polyhedral oligomeric silsesquioxane



Nonreactive organic (R)  
groups for solubilization  
and compatibilization.

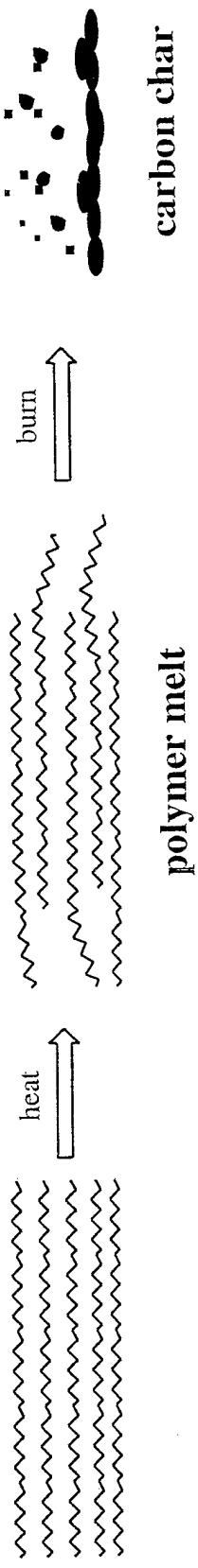


May possess one or more  
functional groups suitable for  
polymerization or grafting.

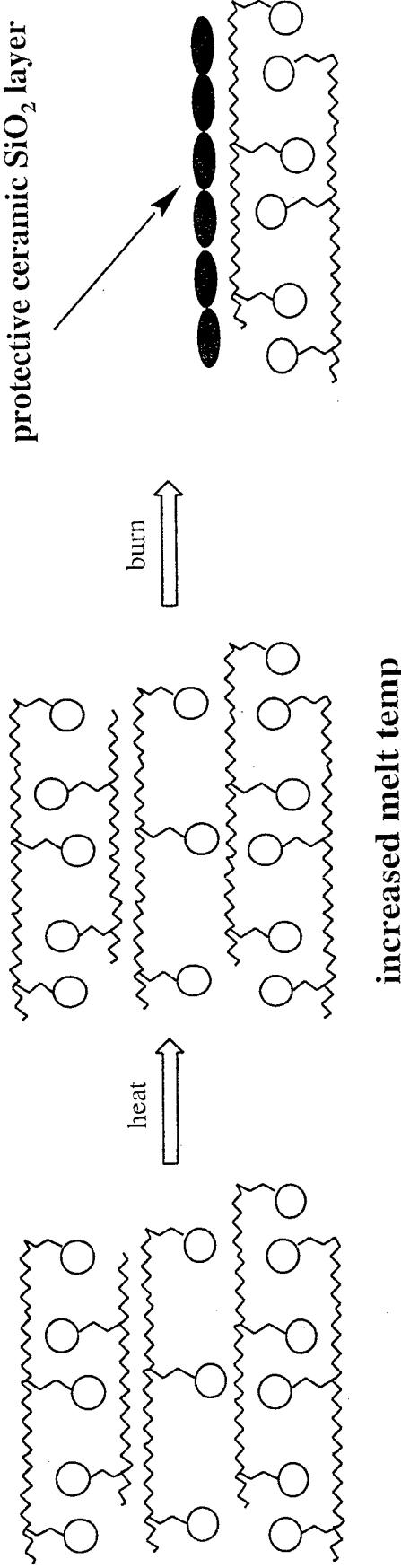
$\text{Si} - \text{Si} = 5.4 \text{ \AA}$   
 $\text{Cp} - \text{Cp} = 15 \text{ \AA}$

# POSS for Low Ablation Materials

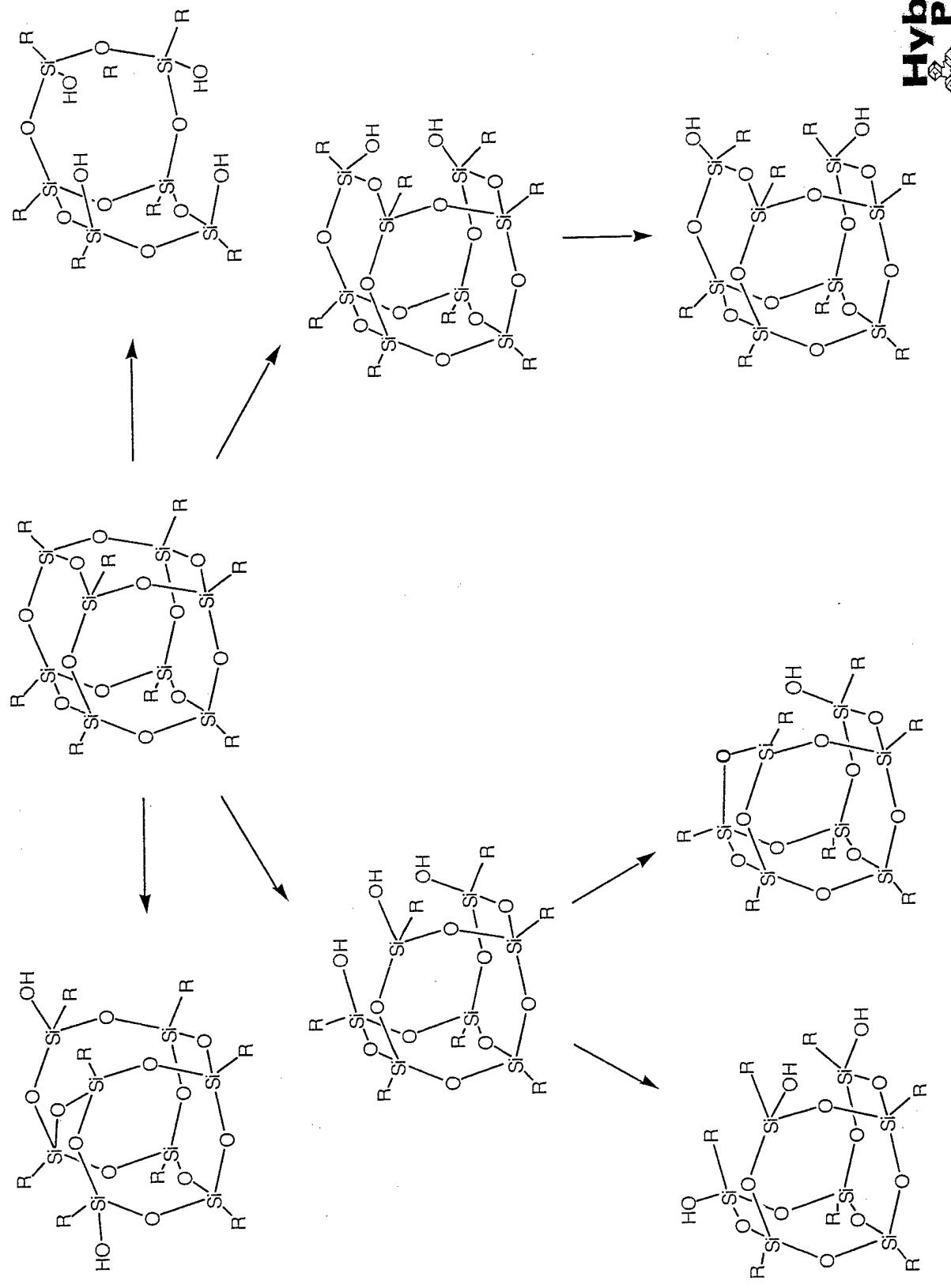
## Traditional Polymer



## POSS Polymer

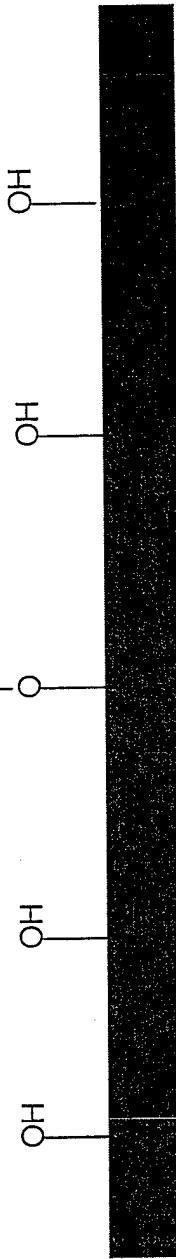
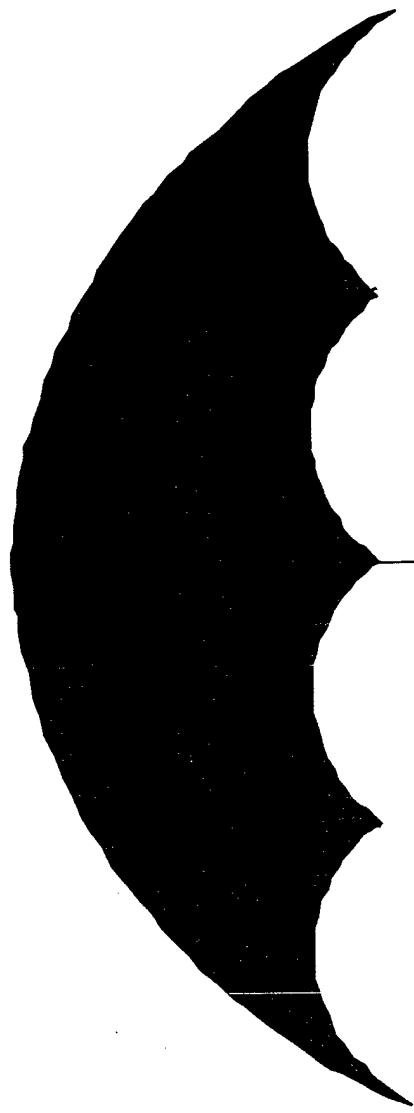


# Stereochemical and Topological Control



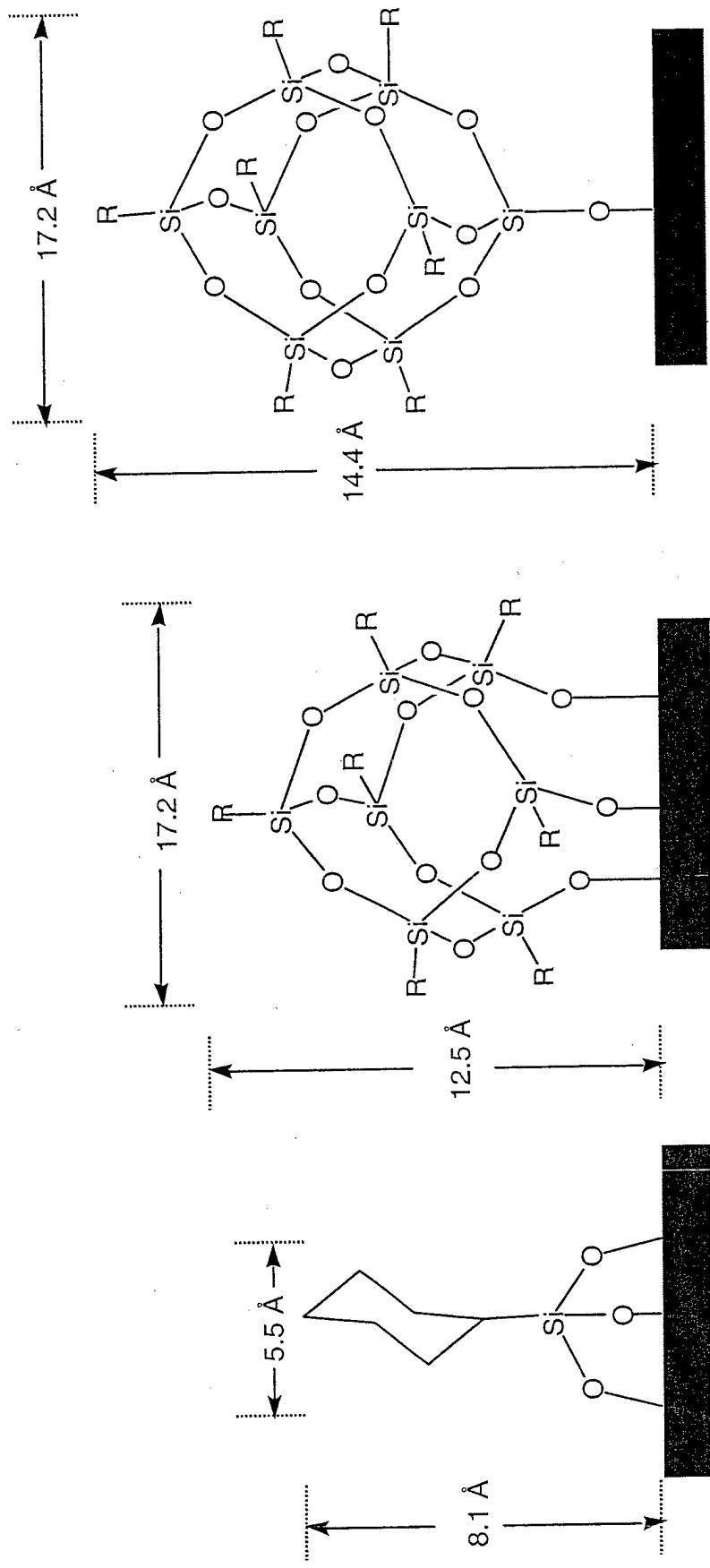
**Hybrid  
Plastics**

## POSS™: The Hydrophobic “Umbrella”



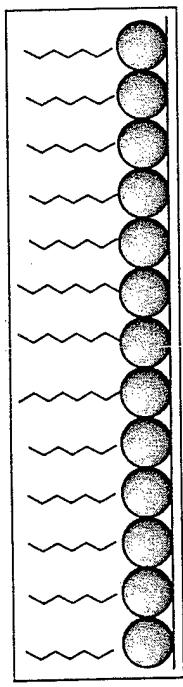
- POSS™ acts as a hydrophobic “umbrella” covering surface Si–OH groups (Approx. 10-12 Si–OH groups/POSS™ nanostructure)
- The surface coverage provided by a single POSS™ cage is approximately 8-10X that provided by a typical silane. (2.32 nm<sup>2</sup> vs. 0.24 nm<sup>2</sup>)

## Silaness vs. POSS™: Monolayer Comparison



- The well-defined polyhedral structure leads to a more well-ordered, regular surface.
- POSS™ cages provide increased surface coverage leading to a more hydrophobic surface.

## States of Monolayer Films

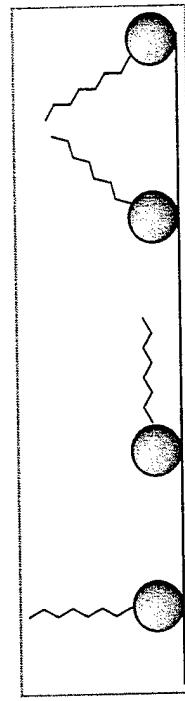
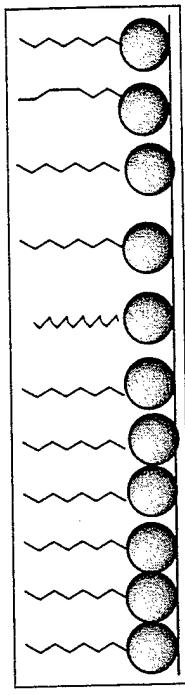
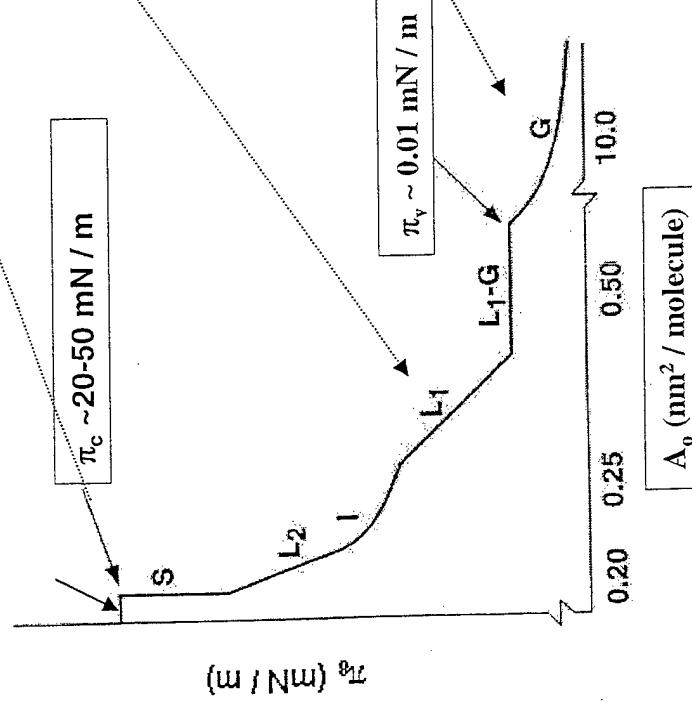


Solid Phase

low compressibility ( $S$ ), nearly linear plot

Liquid Phase

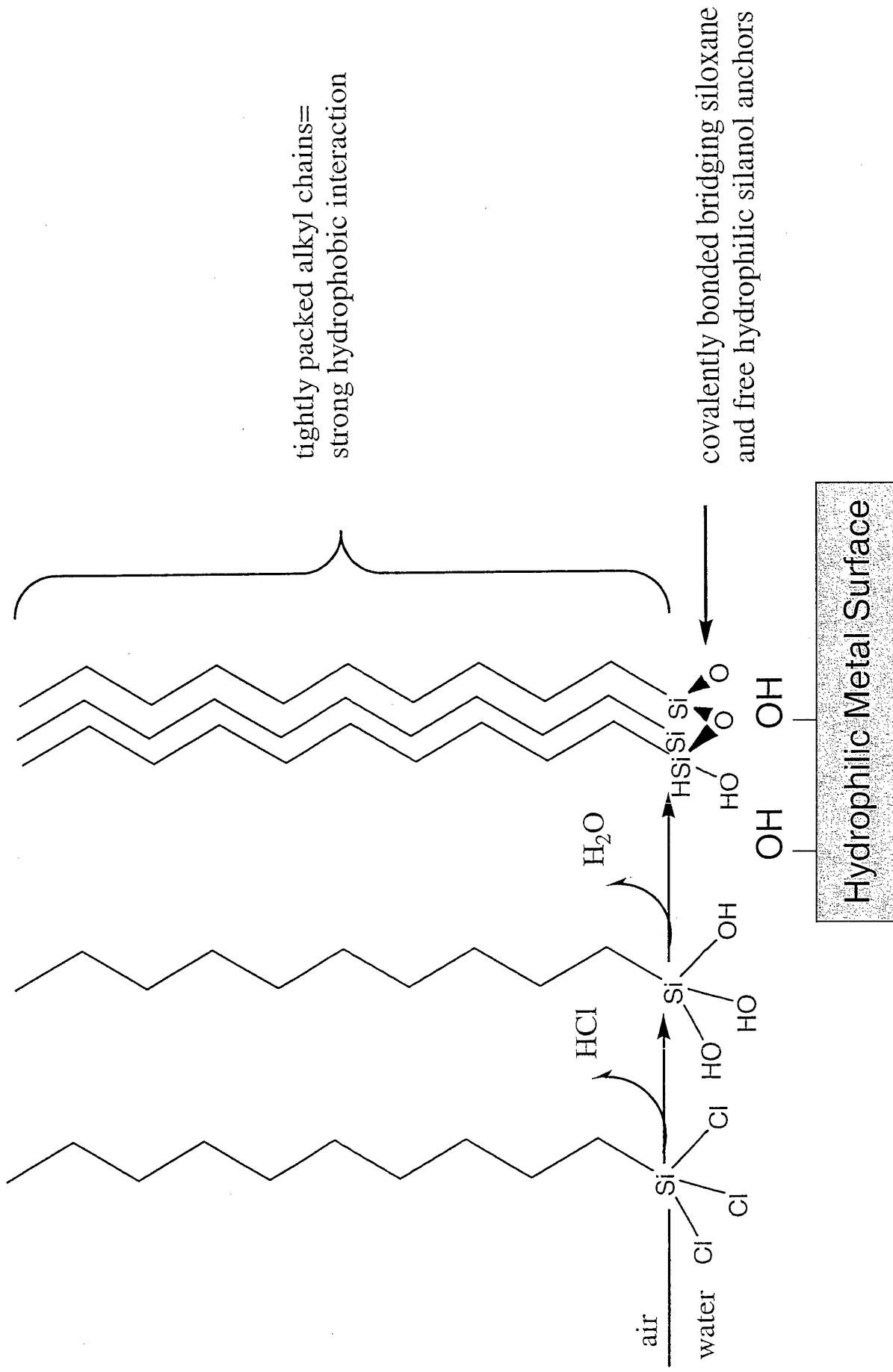
appear as liquid, some disorder in the structure, 2 types— liquid expanded ( $L_1$ ) and liquid condensed ( $L_2$ )



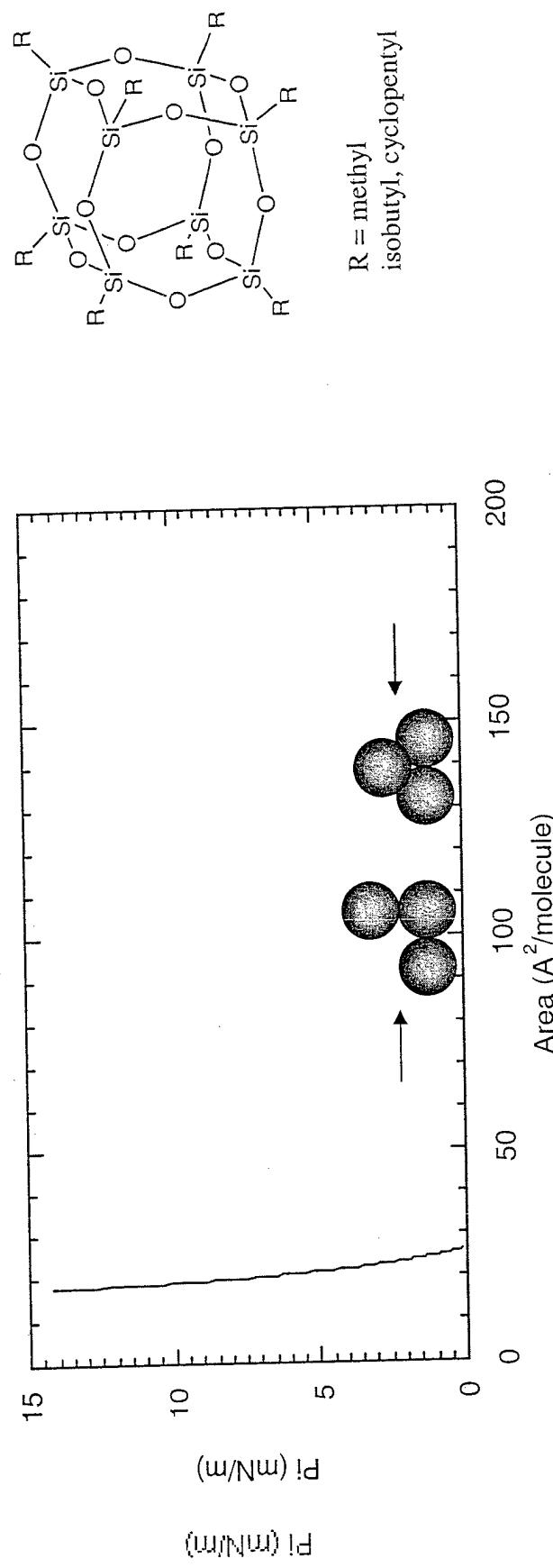
Gas Phase

obey an equation of state,  
area per molecule is large,  $\Pi$   
as low as  $0.001 \text{ mN/m}$

# Chlorosilane Self Assembled Monolayers

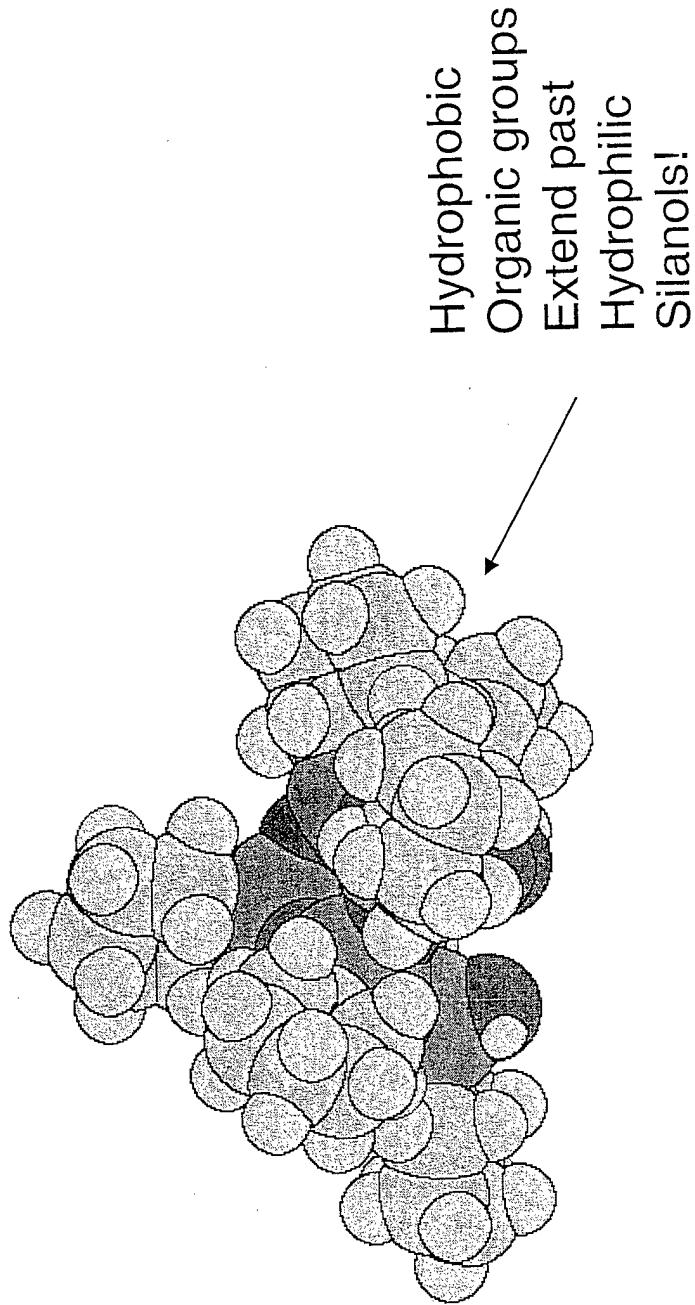


# Fully Condensed POSS Cubes

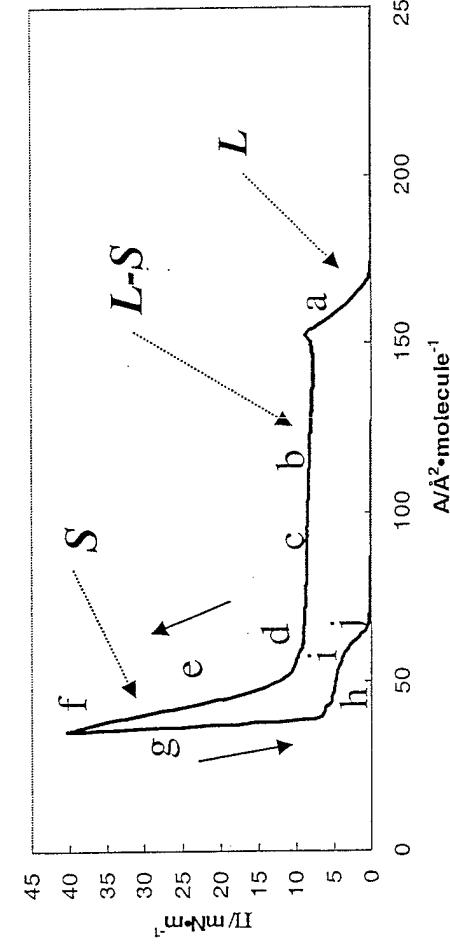
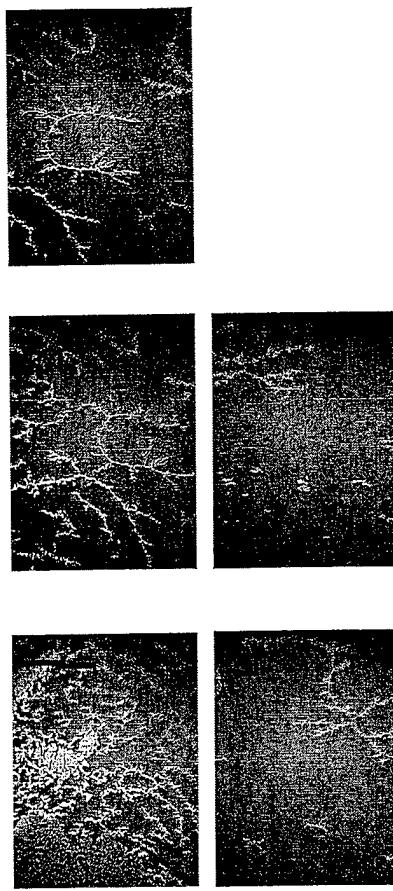
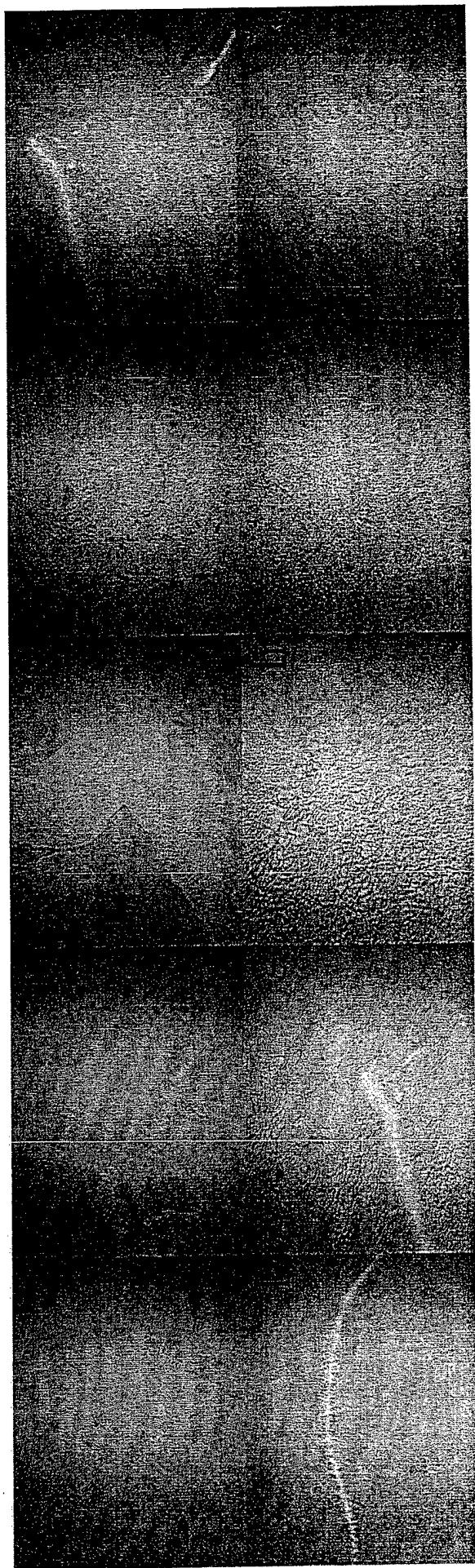


POSS likely exists as aggregates that agglomerate upon compression

## Steric Hindrance of POSS

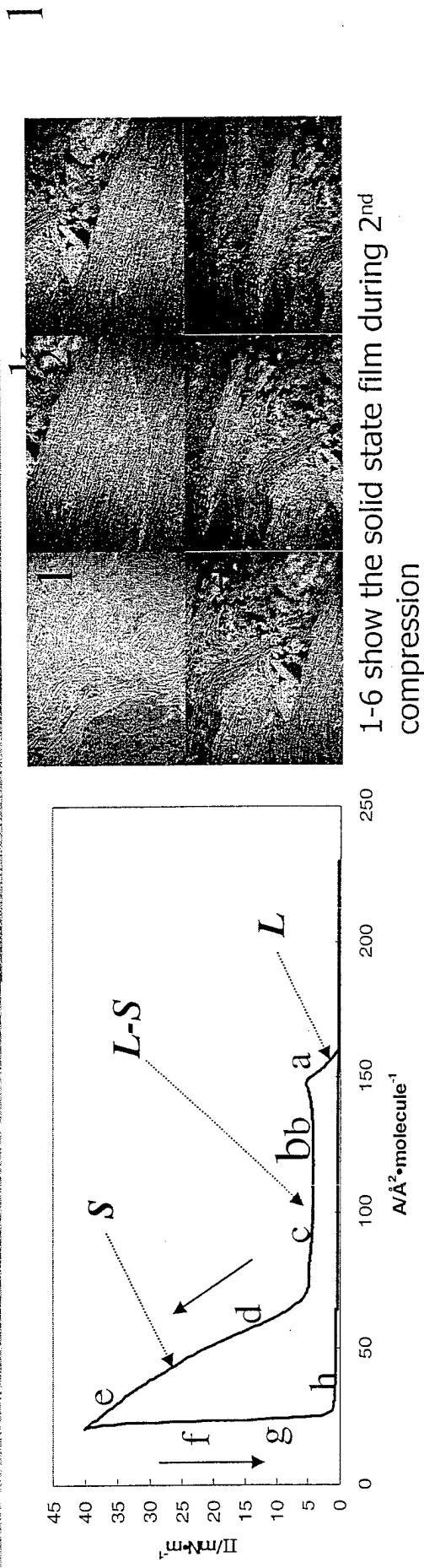
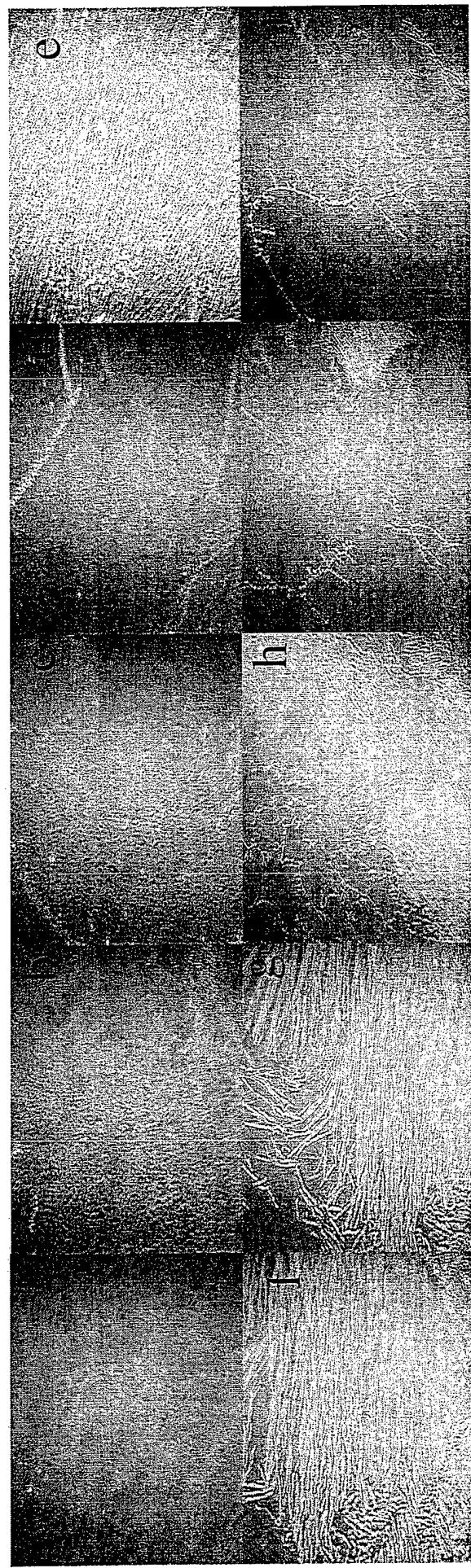


## Cyclopentyltrisilanol-POSS @ 22.5 °C



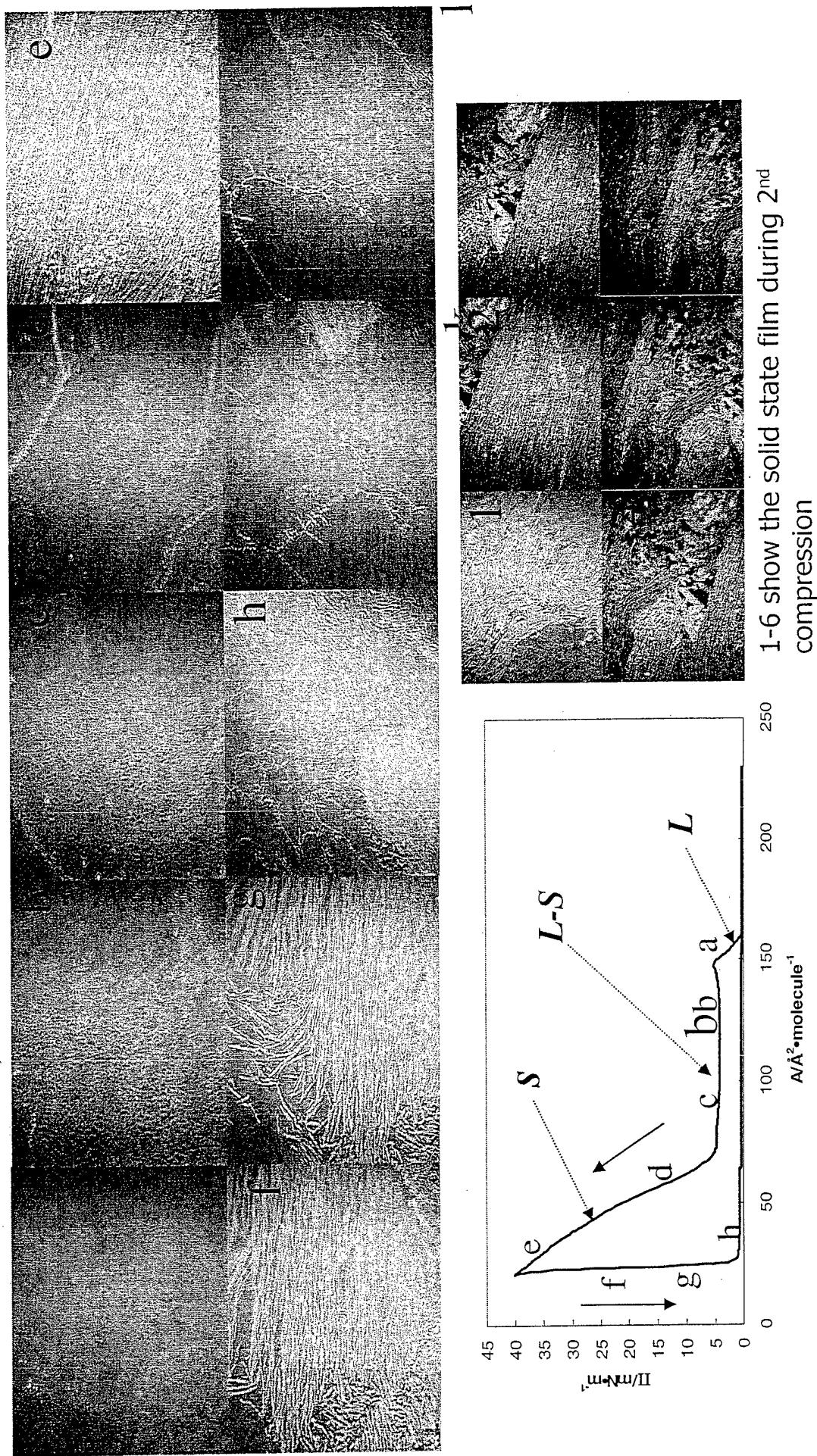
250 1-6 ,dendritic structures obtained during expansion in  
a second compression/expansion cycle

## Cyclohexyltrisilanol-POSS @ 22.5°C

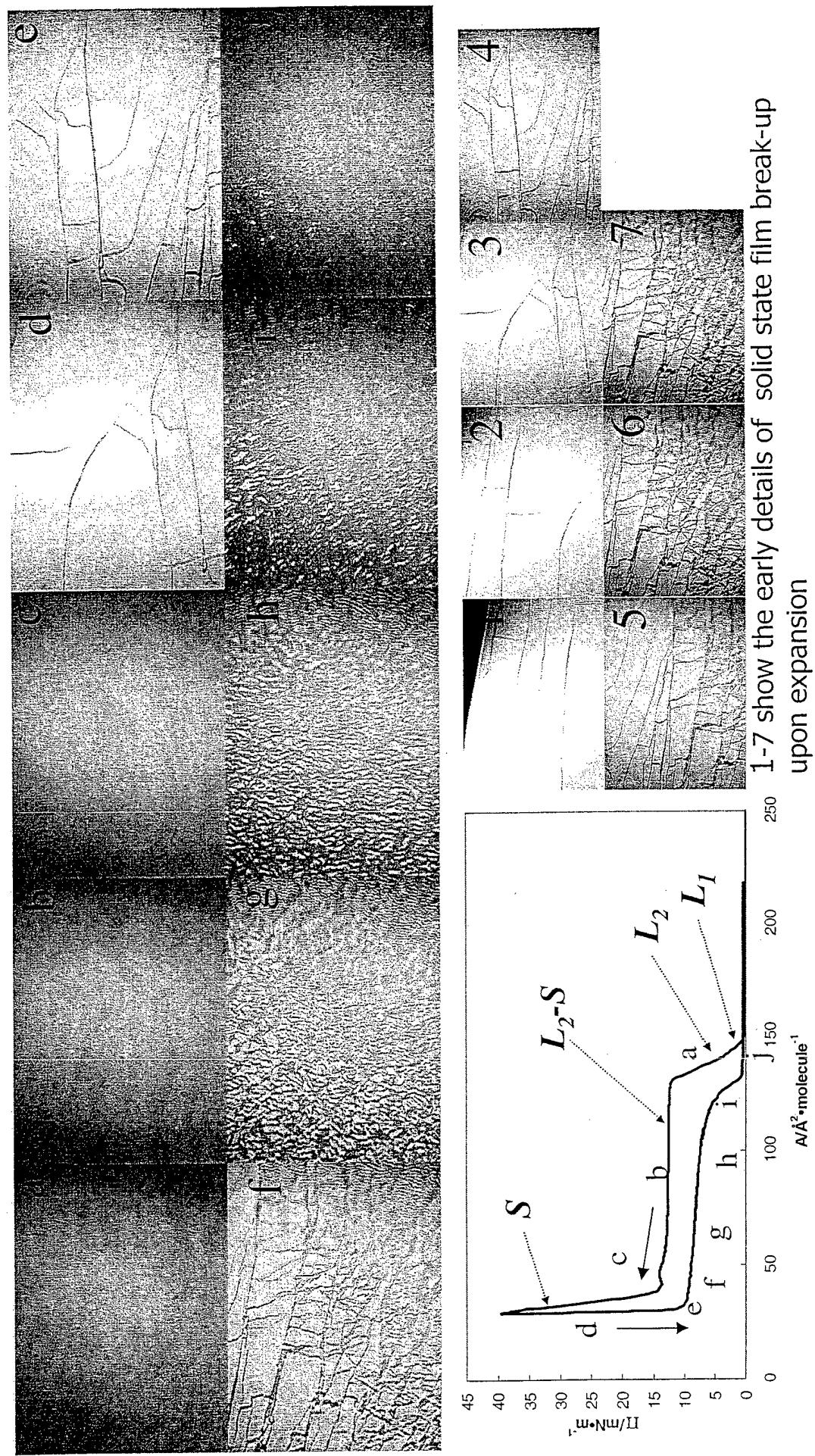


1-6 show the solid state film during 2<sup>nd</sup> compression

## Cyclohexyltrisilanol-POSS @ 22.5°C

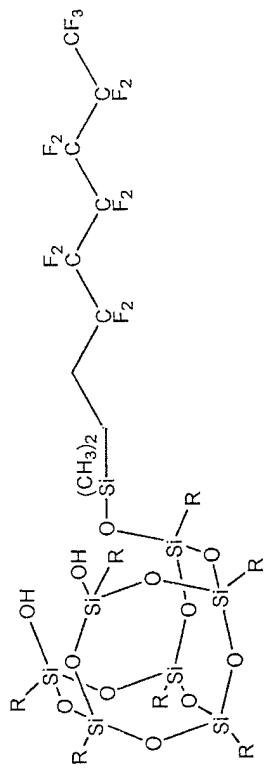


## Phenyltrisilanol-POSS @ 22.5°C



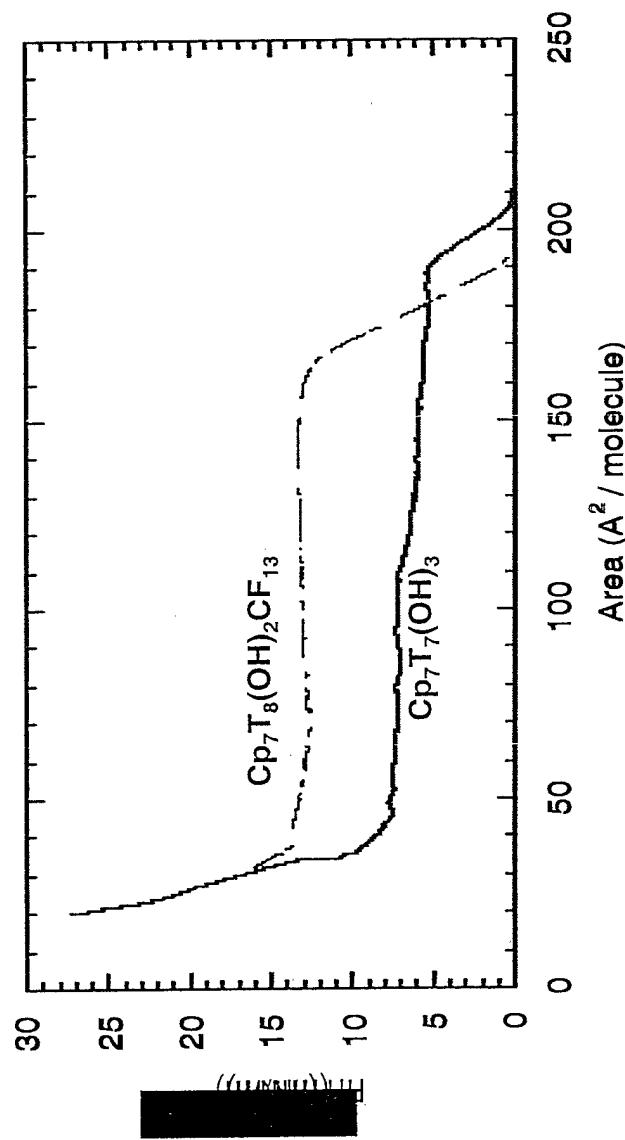
# POSS in a “traditional” surfactant

Quantitative substitution of  
first silanol



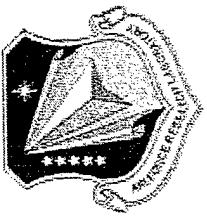
R = cyclopentyl

Pressure-Area  
behavior is very  
similar to POSS  
precursor



## Conclusions

- POSS with hydrophilic silyanol groups can spread to form monolayers on a water surface
- Different POSS geometries (functionality) can change the compression behavior in a Langmuir Blodgett apparatus
- POSS surfactants can have complicated collapse behavior which likely affects the filler behavior (vis a vis aggregation effects)
  - Transfer experiments are underway



## Acknowledgments

- POSS group at AFRL-Edwards (Shawn Phillips, Rusty Blanski, Tim Haddad, Brian Moore, Justin Leland, Pat Ruth, Capt. Rene Gonzalez, Maj. Steve Svejda)
- Hybrid plastics (Joe Lichtenhan, Joe Schwab, Bill Reinerth)
- AFOSR (Dr. Charles Lee), Edwards AFRL-propulsion